

substrate having a dislocation density of  $10^6/\text{cm}^2$  or less as well as the value of FWHM of the X-ray rocking curve from (002) plane less than 80 arcsec, preferably  $10^6/\text{cm}^2$  or less, more preferably  $10^4/\text{cm}^2$  or less.

5        In the supercritical ammono process, we have discovered that A-axis growth is faster 4 times or more than that of C-axis growth and A-axis growth in the supercritical ammono method makes a dislocation density decreased too much in comparison with C-axis growth in the  
10       same supercritical ammono method. Therefore, according to the new aspect of the invention, we can get a template type substrate as shown in Fig.9 wherein the layer A) is a hexagonal shaped substrate having a pair of C-plane surfaces with edge periphery of M-plane having a diameter  
15       of 1 inch or more, which is prepared from a substrate made by A-axis direction growth of bulk mono-crystal nitride in a supercritical ammonium solution containing at least one element of alkali metals. It is suprised that the substrate has a dislocation density of  $10^4/\text{cm}^2$  or less.

20       The substrate according to the present invention is characterized in that even if the gallium-containing nitride layer B) or C) and layers B1) and B2) or C1) and C2) contain at least one element of alkali metals, the content is less than that of the layer A) prepared by  
25       crystallization of nitride in a supercritical ammonium

Fig.2 is a graph showing the change in time of the pressure in the autoclave where  $T=\text{const}$  and illustrates the relation between the changes in the pressure and the processes of dissolution and crystallization in the case of this invention;

Fig.3 is a vertical sectional view of the autoclave and the set of furnaces used for carrying out this invention;

Fig.4 is a perspective view of the apparatus used for obtaining bulk mono-crystalline gallium nitride;

Fig.5 is a graph showing the relationship between the solubility of GaN in the supercritical ammonia which contains potassium amides (with Mineralizer:  $\text{NH}_3=0.07$ ) and the pressure, where  $T=400^\circ\text{C}$  and  $T=500^\circ\text{C}$ ; finally,

Fig.6 is a graph showing the change in time of the temperature in the autoclave for the purposes of this Example.

Fig.7A and 7B are schematic sectional views of the first embodiment of the template type substrate according to the present invention.

Fig.8A and 8B are schematic sectional views of the second embodiment of the template type substrate according to the present invention.

Fig.9 is a schematic plane view showing a process of making A-axis direction growth seed.

a) compounds  $AmBn$ , where A means  $H^+$  and/or metal, preferably alkali,  $NH_4^+$ , Si, S, P, whereas B means halogens, S, P, and n and m mean corresponding stoichiometric coefficients not lower than 1 and/or

5 b) groups of species such as:

- $S_4N_4$ ,  $S_2N_2$ , SN,  $S_4N_2$ ,  $S_{11}N_2$ ,  $P_3N_5$ ,  $P_4N_6$ , PN,
- $PN_2^-$ ,  $PN_{34}^-$ ,  $PN_{47}^-$ ,  $PN^-$ ,  $PN_2^-$ ,
- $PNC_{12}$ ,  $P(NH)_2NH_2$ ,  $P_4S_{10}$ , NP  $(SNH_4)_2$ ,  $NPSNH_4SH$ ,  $NP(SH)_2$ , PNS,

10 Sulfur or silicon species built in the crystalline lattice of the gallium-containing nitride serve as donors; magnesium, zinc or cadmium are acceptors; dopants such as manganese or chromium in the crystalline gallium nitride lattice provide it with magnetic properties; whereas  
 15 phosphor atoms are isoelectronic with respect to nitrogen atoms, and thus they make the energy gap narrower than that in the pure gallium-containing nitride. Those species do not only cause the weakening of ammono-basic nature of the supercritical solvent, but they also modify optical,  
 20 electrical and magnetic properties of the gallium-containing nitride.

Dissolution of the gallium-containing feedstock is a reversible or irreversible process of formation, through the feedstock, of gallium compounds soluble in the  
 25 supercritical solvent, for example gallium complexes.

higher temperature in the crystallization zone than in the dissolution zone. According to the invention, the chemical transport is preferably caused by convection.

**Seed** as it has already been mentioned, is crucial for obtaining desired bulk gallium- or aluminum-containing nitride mono-crystals in a process according to the present invention. In view of the fact that the quality of the seed is crucial for the crystalline quality of the bulk gallium- or aluminum-containing nitride mono-crystals obtained by the process according to the present invention, the seed selected for the process should have possibly high quality. Various structures or wafers having a modified surface can also be used. For example a structure having a number of surfaces spaced adequately far from each other, arranged on a primary substrate and susceptible to the lateral overgrowth of crystalline nitrides may be used as a seed. Moreover, a seed having a homoepitaxial surface, exhibiting n-type electrical conductivity, for example doped with Si, may be used. Such seeds can be produced using processes for gallium-containing nitride crystal growth from gaseous phase, such as HVPE or MOCVD, or else MBE. Doping with Si during the growth process at the level of  $10^{16}$  to  $10^{21}/\text{cm}^2$  ensures n-type electric conductivity. Moreover, a composite seed may be used and in such seed directly on a primary substrate or on a buffer layer made for example of AlN - a

## CLAIMS

1. A substrate used for opto-electric or electrical devices which comprises a layer of nitride grown by means of vapor phase epitaxy growth wherein both main surfaces of the nitride substrate are substantially consisting of non N-polar face and N-polar face respectively and the dislocation density of the substrate is  $5 \times 10^5/\text{cm}^2$  or less.
2. A substrate used for opto-electric or electrical devices according to claim 1, wherein the dislocation density of the nitride substrate is  $10^5/\text{cm}^2$  or less.
3. A substrate used for opto-electric or electrical devices according to claim 1, wherein the dislocation density of the nitride substrate is  $10^4/\text{cm}^2$  or less.
4. A substrate used for opto-electric or electrical devices according to claim 1, wherein the layer B) of nitirde grown by means of vapor phase epitaxy growth is represented by the general formula of  $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ , where  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq x+y \leq 1$ .
5. A substrate used for opto-electric or electrical devices according to claim 1, wherein the layer B) of nitride is represented by the general formula of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  wherein  $0 \leq x \leq 1$ .
6. A substrate used for opto-electric or electrical devices according to claim 1, which comprises a substrate having a thickness of 100  $\mu\text{m}$  or more preferably 150  $\mu\text{m}$  or

more which is sliced from a portion of the layer B2) in the combination layers of A) the layer of bulk mono-crystal nitride containing at least one element of alkali metals (Group I, IUPAC 1989), B1) the layer of nitride grown by means of MOCVD or MBE and B2) the layer of gallium-containing nitride grown by means of HVPE.

7. A substrate used for opto-electric or electrical devices according to claim 1, which comprises a substrate having a thickness of 100  $\mu\text{m}$  or more, preferably 150  $\mu\text{m}$  or more which is sliced from a portion of the layer C2) in the combination layers of A1) the layer of bulk mono-crystal nitride containing at least one element of alkali metals (Group I, IUPAC 1989), B) the layer of nitride grown by vapor phase epitaxy growth, A2) the layer of bulk mono-crystal nitride containing at least one element of alkali metals (Group I, IUPAC 1989), C1) the layer grown by means of MOCVD or MBE and C2) the layer of gallium-containing nitride grown by means of HVPE.

8. A substrate used for opto-electric or electrical devices according to claim 1, wherein the substrate is a gallium-containing nitride containing silicon (Si) or oxygen (O) as donor dopants.

9. A substrate used for opto-electric or electrical devices according to claim 1, wherein the substrate is a gallium-containing nitride containing magnesium (Mg) or

zinc (Zn) as acceptor dopants.

10. A substrate for opto-electric or electrical devices according to claim 8 or 9, wherein the concentration of dopants ranges between  $10^{16}/\text{cm}^3$  and  $10^{21}/\text{cm}^3$ .

5 11. A process of preparing a substrate for opto-electric or electrical devices which comprises steps of:

(a) preparing a layer A) of bulk mono-crystal nitride containing at least one element of alkali metals (Group I, IUPAC 1989) to have a thickness for substrate by  
10 crystallization of gallium or aluminum-containing nitride on a seed from a super-critical ammonia-containing solution; (b) forming a layer B) or C) of nitride by means of vapor phase epitaxy growth on Al or Ga-polar face of the layer A);

15 and (c) slicing the layer B) or C) off from the substrate A) to get a substrate having a thickness of 100  $\mu\text{m}$  or more and a main surface substantially consisting of Al or Ga-polar face.

12. A process of preparing a substrate for opto-electric  
20 or electrical devices, wherein the step (b) comprises (b1) forming a layer B1) or C1) of nitride by means of vapor phase epitaxy growth on Al or Ga-polar face of the layer A) and (b2) forming a layer B2) or C2) of nitride by means of vapor phase epitaxy growth on the layer B1) or C1);

25 and (c) slicing the layer B2) or C2) off from the substrate

A) to get a substrate having a thickness of 100  $\mu\text{m}$  or more and a main surface substantially consisting of Al or Ga-polar face.

13. A process of preparing a substrate for opto-electric  
5 or electrical devices, which further comprises (d) forming a layer D) of nitride by means of vapor phase epitaxy growth on Al or Ga-polar face of the layer B), C), B2) or C2).

14. A process of preparing a substrate for opto-electric  
10 or electrical devices, which further comprises (d) forming a layer D) of nitride by means of vapor phase epitaxy growth on Al or Ga-polar face of the layer B), C), B2) or C2);

and (e) slicing the layer D) off from the substrate B), C),  
15 B2) or C2) to get a substrate having a thickness of 100  $\mu\text{m}$  or more and a main surface substantially consisting of Al or Ga-polar face.

15. A process of preparing a substrate for opto-electric  
or electrical devices, according to any one of claims 11 to  
20 14, wherein the layer B), B1), C) or C1) is prepared by MOCVD and has a thickness of 0.1 to 3  $\mu\text{m}$ .

16. A process of preparing a substrate for opto-electric  
or electrical devices according to claim 15, which  
comprises further step of polishing one of the faces of the  
25 layer B), B2), C) or C2) to get a substrate for vapor phase



epitaxy.

17. A process of preparing a substrate for opto-electric or electrical devices according to any one of claims 11 to 16, which comprises further step of annealing the substrate B), B2), C) or C2).in the atmosphere that does not contain hydrogen but does contain at temperature between approx. 600 and 1050°C, thus producing material with better crystalline quality than before the annealing.

18. A process of preparing a substrate for opto-electric or electrical devices according to any one of claim 17, wherein the step of annealing is carried out in the atmosphere of inert gas with an addition of oxygen between 10 and 30 vol.%.

19. A process of preparing a substrate for opto-electric or electrical devices according to claim 17, wherein the the step of annealing is carried out in a single step or in multiple steps until the desired level of impurities (such as hydrogen and/or ammonia or ions formed from the impurities formed during the crystallization and/or annealing process) is reached.

20. A process of preparing a substrate for opto-electric or electrical devices according to any one of claims 11 to 19, which comprises further step of removing impurities from bulk mono-crystalline nitride by a process of rinsing in the environment of supercritical ammonia-containing

solvent, water or carbon dioxide or being subjected to the action of gaseous hydrogen, nitrogen or ammonia.

21. A process of preparing a substrate for opto-electric or electrical devices according to claim 20, wherein the step  
5 of rinsing is carried out with aid of the application of ultrasounds or the exposure to an electron beam.

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